



**FINAL REPORT ON PHASE SPECIATION OF PU AND AM FOR
'ACTINIDE MIGRATION STUDIES AT THE
ROCKY FLATS ENVIRONMENTAL TECHNOLOGY SITE'**

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Significant Findings in FY00:

- 1) **Actinide Phase Speciation:** Total $^{239,240}\text{Pu}$ and ^{241}Am concentrations in the storm runoff and pond discharge samples were below the discharge limit of 0.15 pCi/L. Both Pu and Am activity concentrations in storm runoff (GS10 on 5/8/00) and pond discharge (GS03 on 4/27/00) samples were also comparable to those determined in 1999 samples from Walnut Creek at GS03. Both storm runoff and pond discharge sampled this year showed again a substantial fraction of Pu and Am in the 0.5 μm filter-passing fraction. The majority of Pu and Am in the 0.5 μm filter-passing fraction was colloidal, i.e., it was filtered out by 100kDa or 3kDa ultrafilters using cross-flow ultrafiltration (CFUF), with only a small fraction of the 0.5 μm filter-passing Pu and Am passing a 3 kDa ultrafilter. Pu activity concentrations in the particulate fractions ($>20 \mu\text{m}$ & $0.5\text{-}20 \mu\text{m}$) amounted to about 90% of the total.
- 2) **Colloidal Pu remobilization during soil erosion:** Pu concentrations above the action level ($\geq 0.15 \text{ pCi/L}$) occur predominantly during storm runoffs in early spring and summer. During these events, elevated concentrations of colloidal Pu, accompanying those in the particle phase, are being observed (Santschi et al., 1999). We hypothesized that colloidal Pu, as a pseudo-colloid (i.e., Pu associated with a different carrier phase), is generated by soil erosion and transport, and that remobilization of colloid-bound Pu during soil erosion events is likely aided by elevated concentrations of humic acids in soil waters. During this funding year, we tested this hypothesis in soil resuspension experiments with RFETS soils, and demonstrated that there is a close relationship between the remobilization of colloidal Pu ($\leq 0.4 \mu\text{m}$) and the dissolved organic matter (DOM) concentration (i.e., humic acids) in the water at environmentally relevant concentrations. We furthermore observed a kinetic effect, i.e., an increasing colloidal Pu concentration at increasing resuspension time, and a particle-concentration effect, i.e., a decreasing phase partition coefficient of Pu ($R_p \{\text{in L/kg}\} = \text{ratio of particulate concentration \{in pCi/kg\} to the filter-passing concentration \{in pCi/L\}}$) with increasing particle concentration (C_p , in kg/L), as $\log(R_p) = 3.2 - 0.74 \log(C_p)$. Which of these factors is dominant in the field would require further analysis of field data.
- 3) **Colloid Composition:** Isoelectric focusing of ^{14}C radiolabelled colloids showed again that they contain strong acid functional groups which impart the organic fraction a negative charge at natural pH's. Bulk colloidal matter contains also strong basic functional groups, as was evident from ^{59}Fe labeling experiments. Colloids isolated from the pond discharge and storm runoff samples contained about 3 to 12 % organic carbon, 0.02 to 1 % Fe, and 0.02 to 1.3 % Al, with the higher value for the GS10 sample from 5/8/00. These values agree with their predominantly inorganic nature. The clay- and organic carbon - rich nature of the colloids was corroborated by additional Scanning Transmission Electron Microscopy (TEM) and Energy Dispersive Spectroscopy (EDAX) images, which also suggest that GS10 colloids contain larger amounts of Fe-rich colloids.

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- 4) Particle and Th(IV) residence times in Pond B-5: Measurements of Th(IV), as an analogue of Pu(IV), in total, dissolved and particulate fractions of Pond B-5 water resulted in estimates of how long, on the average, it would take for a four-valent ion to be scavenged and removed from the water. Th(IV)-scavenging and particle residence times, derived from measurements of $^{238}\text{U}/^{234}\text{Th}$ disequilibria in the water, were of the order of a few hours to one day, respectively, supporting the effectiveness of the ponds in reducing particle and Pu loads. From these results, we would predict that at water residence times in excess of one to a few days, most of the Pu and particle load entering a pond would be removed to the sediments. Water residence times are currently more than a month. If holding ponds were to remain, they should be designed with water residence times of more than a few days to maximize their effectiveness in reducing particle and actinide loads to down stream sites.

1. Overview, Questions and Hypothesis

The goal of the Actinide Migration Evaluation (AME) is to provide data in support of Site closure, including: 1) soil action levels vis-à-vis surface water quality; 2) long-term disposition of the ponds; 3) 'far-field' actinide behavior during long-term closure.

Four broad areas of investigation emerged from group discussions with AME members and site personnel for consideration for FY 2000 work:

- 1) Phase speciation studies of actinides in surface waters;
- 2) Colloid characterization studies;
- 3) Studies of colloid generation during simulated soil erosion (i.e., soil resuspension) events;
- 4) Determination of in-situ removal time studies for particles and colloids in ponds.

The following question was addressed in the FY2000 research: What causes exceedances of Pu and Am concentrations in RFETS surface waters, which often are associated with storm runoff?

The following Hypothesis was tested in the FY2000 research: The elevated concentrations are related, besides hydrodynamic conditions (i.e., storm surface runoff vs base flow), to the nature and types of organic matter present in soils, stormwater and pond water at the time of sampling. Organic matter can modify the surface charge and characteristics of particle and colloid aggregates. On the one hand, humic and fulvic acids can impart a negative surface charge to particles and colloids, which can promote disaggregation and dispersion of aggregates, and thus, increased mobility and concentrations of colloidal species in surface waters. On the other hand, large, surface-active, organic molecules such as exopolymeric acid polysaccharides from bacteria and algae, act to bind colloidal and particulate species together, and thus, cause their removal and lower their concentrations in surface waters.

2. Justification

A wide range of work at Rocky Flats has demonstrated that 'particulate' and 'colloidal' forms of Pu and Am make up a significant fraction of actinides in surface waters and suggests that surface water transport of Pu and Am is dominated by aggregation and disaggregation processes of particles and colloids during soil erosion events. A clear understanding of the phase speciation of Pu is a prerequisite for the development of defensible closure strategies. Questions concerning the environmental form of Pu and Am have direct bearing on evaluating the importance of various migration pathways and in the development and refinement of Data Quality Objectives (DQO: i.e., model parameters and uncertainty levels).

3. Tasks

3.1 Task 1: Colloid and particulate associations of Pu and Am

In FY2000 we continued the phase speciation work of Pu and Am in stream water, using the sites already investigated in 1998 and 1999.

3.1.1 Objectives:

1. To determine the association of Pu and Am with: 1) particulate, 2) colloidal and 3) dissolved phases for field samples from a selected pond, pond release waters and a future compliance point.
2. To determine if natural organic matter plays a role in the formation of colloids that facilitate transport of actinides from contaminated soil source terms.
3. To determine the chemical nature of the colloidal carrier phase (e.g., Fe, Mn, C, Al, etc.).

3.1.2 Justification:

FY 98&99 work has demonstrated that 0.5 μ m filter-passing Pu is predominantly in a colloidal form. The issue of the speciation of filter-passing forms of Pu is crucial for understanding of transport, i.e., the relationship between surface water quality and soil action levels, as well as to evaluate the scientific defensibility of RESRAD model simulations. The distribution of Pu and Am among different particles sizes and colloid molecular weights is important for developing management controls on surface water quality.

3.1.3 Analytical Plan:

Phase association studies of Pu and Am investigations involved the following subtasks:

- a) Surface water sampling by CFUF,
- b) Colloid isolation and characterization,

The selected sampling sites were Pond B-5, pond release waters at compliance point GS03: Walnut Creek at Indiana Street, and stormwater runoff at GS10, South Walnut Creek at the B-

series bypass (Figure 1). Grab samples were collected by bailing water from the stream using a small container followed by compositing the water into clean 15 to 20 Liter Nalgene carboys for processing and analysis in the laboratory (Figure 2). In addition, soil samples were collected for extraction of natural organic matter fractions and used in the soil erosion/colloid stability experiments at Texas A&M University at Galveston (TAMUG).

The methods for isotope separation were adapted from EPA Method 908.0 (1980), USDOE (1979), USEPA (1979), and Yamato (1982) as described also in (Appendix 2). Each sample was acidified with concentrated nitric acid to pH <2 and allowed to sit for at least 16 hours. For each sample concentrated hydrochloric acid was added at 5ml/L and ^{243}Am and ^{242}Pu yield tracers were added. The samples were placed on a stir plate and 5 ml of 40 mg/ml Fe(III) carrier was added. The pH was measured and concentrated hydrochloric acid added until pH is <1. The sample was covered and stirred for 30 minutes and the pH measured again.

Once the pH was <1, concentrated ammonium hydroxide was added until turbidity remained constant then an additional 50 mls was added. The sample was again covered and stirred. After 30 minutes, the sample was removed from the stir plate, the stir bar removed and the precipitate was allowed to settle. The supernate was decanted until the precipitate slurry could be transferred to 250 ml centrifuge tubes. The samples were centrifuged for 30 minutes at 3000 rpm. The supernate was decanted and the precipitate was shipped to TAMUG. At TAMUG, the samples were dissolved in concentrated HCl to which 75 ml of 9 N HCl and 2 ml saturated sodium nitrite were added. The samples were then run through a series of three anion exchange columns (Appendix 2). The first column separated the Am from the Pu fractions. The Pu was then microprecipitated on a filter, mounted on a stainless steel planchet and alpha counted. The Am fraction was carried through a methanolic anion exchange column followed by a TEVA resin column. The Am fraction was microprecipitated, mounted on a stainless steel planchette and alpha counted.

The protocols of Guo and Santschi (1996,1997) and Wen *et al.* (1996, 1999) were followed for isolating colloidal and particulate phases of metals such as Pu, Am from surface waters by CFUF. Chemical parameters measured in the aqueous sample fractions were:

- total organic carbon (TOC),
- dissolved organic carbon (DOC),
- colloidal organic carbon (COC),
- particulate organic carbon (POC),
- pH,
- alkalinity, and
- Al, Fe and Mn.

Chemical parameters measured in the filtered solids (colloid and particulate phases) were:

- % organic carbon,
- Al, Fe and Mn

Aliquots of colloid and particle samples were kept for TEM imaging analyses. These analyses were used to visually identify the gross composition of the particulate and colloidal phases. In selected cases, electrophoretic focusing experiments (Quigley, 2000) determined isoelectric points of isolated colloids. *A note on terminology:* We denote all fractions with either the upper or lower size or nominal molecular weight cutoff limit, or both. The terms "dissolved", "filtrate" are ambiguous, and the terms "retentate" and "permeate" are reserved for fractions which were retained by or had permeated an ultrafilter.

3.1.4 Strategy:

Surface water samples from the field were taken in an extended sampling expedition in April/May 2000. Laboratory processing of samples was carried out in the following months.

3.2 Task 2: Resuspension/Colloidal Pu release experiments

The laboratory experiments involved treatment of actinide-contaminated soil with commercial and extracted, natural organic matter to investigate natural mechanisms of colloid formation during storm water runoff.

3.2.1 Objectives:

1. To determine if natural organic matter plays a role in the formation of colloids that facilitate transport of actinides from contaminated soil source terms.
2. To experimentally determine what natural processes favor particle and colloid stabilization or destabilization using experimental approaches given in Wilkinson et al. (1997).

3.2.2 Justification:

A better understanding of the process(es) which control the speciation of filter-passing forms of Pu is crucial for evaluating their transport. A major focus of this task is to determine the dominant Pu species generated via resuspension during storm runoff. Some of the major processes which control colloid formation will be studied in controlled laboratory experiments, with the purpose of relating colloid stability to organic matter composition. The type of natural organic matter can control the tendency of particles and colloids to aggregate. For example, small organic molecules such as fulvic acid and other organic acids can increase dispersion of soil colloids through their effect on particle charge, while large, surface-active, organic molecules such as polysaccharides act to bind colloid particles together (e.g., Gu and Doner, 1993; Kretzschmar et al., 1997; Wilkinson et al., 1997). Colloid stability is an important colloid characteristic because it reflects the extent to which colloidal material interacts with particles and immobile soil media. Therefore, colloid stability is a primary parameter for 1) estimating colloid mobility and for 2) development of engineering and management strategies for removing colloidal-associated actinides from surface water.

3.2.3 Analytical Plan:

Colloid formation and associated actinide partitioning was investigated in controlled soil resuspension experiments. The soil was first sieved through a 1mm sieve to reduce inhomogeneity of the Pu activities. This fine soil fraction was added to a teflon jar containing 0.5µm filtered tap water which was rapidly stirred using a stir bar on a stir plate. The resuspension experiments were carried out with variable amounts of commercial organic matter compounds (i.e., Aldrich humic acids, exopolymers of microorganisms, such as Alginic Acids, Xanthen) and soil extracts (e.g., humic acids). Pu-contaminated soils from the Site were resuspended in the presence or absence

of these natural organic substances and then 0.45 μ m filtered. In select cases the filtered fraction was fractionated further using 1kDa stirred cell ultrafiltration to determine if Pu colloid formation occurs (Table 17). The solutions were analyzed for DOC, Pu and Am to determine whether colloid formation also liberated Pu and Am from the soils. A schematic of these experiments is displayed in Figure 3. Pu-contaminated soil in 0.5 μ m filtered tap water served as a control.

3.2.4 Strategy:

The strategy was to carry out these soil resuspension and colloid remobilization experiments using existing samples. Laboratory processing of these samples was carried out throughout the year.

3.3 Task 3: In-situ particle and colloid residence time determination

We determined in-situ particle and colloid residence times in pond waters using the $^{234}\text{Th}/^{238}\text{U}$ disequilibrium technique (e.g., Baskaran et al., 1996; Guo et al., 1997; Santschi et al., 1999a).

3.3.1 Objective

To investigate if in-situ particle and Th(IV) residence time determination in pond waters using the $^{234}\text{Th}/^{238}\text{U}$ disequilibrium technique prove to be feasible.

3.3.2 Justification:

FY 98&99 work has demonstrated that 0.5 μ m filter-passing Pu is predominantly in a colloidal form. Colloid stability is a primary parameter for 1) estimating colloid mobility and for 2) development of engineering and management strategies for removing colloidal-associated actinides from surface water. Particle and colloids residence times in ponds are likely short, as actinides are removed to better than 90% in the pond water in about 45 days, according to Site sources. Better knowledge of residence times of particles and colloids would facilitate a future decision about pond operations.

3.3.3 Analytical Plan:

Because ^{238}U concentrations were high enough (i.e., 1 dpm/l, or higher), and relatively constant over time, the $^{234}\text{Th}/^{238}\text{U}$ disequilibrium technique (e.g., Baskaran et al., 1996; Guo et al., 1997; Santschi et al., 1999a), it can provide estimates of particle and colloid residence times at steady state based on the deficiency of ^{234}Th with respect to its mother nuclide, ^{238}U , in particle, colloid and solution phases. Large volumes (600 to 1100L) of water were pumped from the ponds through a prefilter (changed three times during filtration) and two MnO_2 impregnated fiber filters, which efficiently extract ^{234}Th . The efficiency of extraction is determined from the activity ratio in the two cartridges, and is usually over 90% (Baskaran et al., 1993).

3.3.4 Strategy:

Surface water samples from Pond B-5 were taken in a sampling expedition in April 26-27 by pumping water through extractor cartridges in the field. Laboratory processing of samples was carried out in the month following sampling.

4. RESULTS AND DISCUSSION

We sampled, filtered, ultra-filtered and processed a discharge sample on 4/27/00 and a storm runoff sample on 5/8/00, in duplicate. For the discharge sample, approximately 200 liters of water were taken from GS03 and brought in various containers to CSM, where it was combined in a 55 gallon drum, which had been pre-cleaned with Radiacwash (a detergent). The 200 liters of storm runoff were collected from GS10 and brought to Colorado School of Mines (CSM) in two 55 gallon drums, which had been pre-cleaned with Radiacwash. Both samples were size fractionated in duplicate for a total of 4 samples of approximately 90 liters each. 12 - 18 liters of total water (unfiltered) was set aside for each sample. The remaining water was passed through 20 micron and 0.5 micron filters and collected in 5 gallon carboys. The 5 gallon carboys used to take sub-samples from the drums had been washed with Radiacwash, as well as with acid. One carboy of 0.5 micron filtered water was set aside for later analysis of the 0.5 micron filter passing fraction. The remaining 0.5 micron filtered water was used for the cross flow ultrafiltration (CFUF). Thirty to forty liters were run through a 3 kDa filter membrane and another thirty to forty liters were run through a 100 kDa filter membrane. All size fractions were processed by $\text{Fe}(\text{OH})_3$ precipitation at CSM. The resultant precipitate was sent to TAMUG for radiochemical analysis of $^{239,240}\text{Pu}$ and ^{243}Am .

In another experiment, Pond B-5 was sampled 4/26/00 and 4/27/00 for ^{234}Th and ^{238}U to calculate residence times of the particulate and filter-passing phases. Th-234 was extracted by pumping hundreds of liters of water through a 0.5 μm prefilter and two 0.5 μm MnO_2 impregnated cartridge filters. Filters were then combusted in a muffle furnace and the ash was packed into counting vials and counted on a well Ge gamma detector. ^{238}U was determined by ICP-MS.

At TAMUG, soil resuspension experiments were also conducted using Rocky Flats soil (99A3372-002.006) as a source of Pu to the water. Soil concentrations, resuspension times, as well as type and quantity of organic substances were varied to assess colloid formation effects on $<0.45\ \mu\text{m}$ filter-passing $^{239,240}\text{Pu}$ activities.

4.1. Pu and Am concentration and phase speciation data from pond and storm discharge samples:

$^{239,240}\text{Pu}$ and ^{241}Am phase speciation results are shown in Tables 1a, 1b and 2, and ancillary results in Tables 3-11. Unfortunately, in the first pond discharge sample (A), Pu and Am activities in the 3kDa ultrafiltration samples were anomalous. The problem was attributed to the tracer not having equilibrated with the sample, likely due to interference by organics. To alleviate the organic matter problem, all subsequent samples were treated with strong acids (HCl and HNO_3) first, and evaporated after tracer addition prior to the column chemistry. The second pond discharge sample (B), gave more reliable results, as judged from the Pu activity balance.

The data used for Figures 4-6 are summarized in Table 2. Sample 'B' was used for the particulate values with the total being the sum of the measured fractions for Pu and the $>20\mu\text{m}$ being calculated by the difference between the measured total and the other fractions. For the $<0.5\mu\text{m}$ fractions, average values were used where feasible. For the 100kDa - $0.5\mu\text{m}$ fraction, the measured 100kDa container and cartridge acid wash was added to the measured 100kDa - $0.5\mu\text{m}$ fraction. The 3-100kDa was calculated by difference (sum of $<0.5\mu\text{m}$ fractions - $<3\text{kDa}$ - 100kDa- $0.5\mu\text{m}$).

As had been observed in previous years, most of the Pu and Am in the water (Tables 1a & 1b, Figures 4-6) was found in the particulate phase, with most of the remainder in the colloidal phase. Pu/Am ratios (Table 12) of the different phases and samples indicate that the storm runoff samples generally had lower ratios than the pond discharge samples. Values of phase partition coefficients, R_p , range from 4.8 to $8.0 \cdot 10^4 \text{ L/kg}$ (Table 13).

4.2. Colloid characterization:

ICP-MS, CHN, isoelectric focusing and TEM were used for characterizing freeze-dried colloids from the April and May sampling expeditions. As in previous years, colloids were primarily composed of clay and organic matter colloids (0.02-1 % Fe, 0.02-1.3 % Al, 3.1-11.9 % OC, see Tables 8, 9). Colloids from the storm discharge contained higher Al, Fe, Mn (Table 9), and %OC (Table 8). The same was true for % OC in suspended particulate matter (Table 4).

Colloids were radioactively tagged with ^{14}C and ^{59}Fe (^{14}C -Dimethyl sulfate on the -OH sites of sugars ^{59}Fe on -OH sites of Fe oxyhydroxides and clay minerals), using protocols given Wolfenbarger and Crosby (1983). The labeling is a methylation reaction and labels mainly the hydroxyl groups of both neutral and amino sugars (Wolfenbarger and Crosby, 1983). The ^{14}C radiolabeled organic matter was stored in dH_2O in a sterilized bottle at 4°C . Generally, both isotopes were added to a small aliquot of colloids in a batch reactor. Each isotope were measured in the different filter fractions separately using liquid scintillation counting, LSC. Small volumes (100 μl with approximately 20 nCi ^{14}C) of ^{14}C or ^{59}Fe radiolabeled colloids were then used in isoelectric focusing gel electrophoresis experiments (Figure 7, Table 14). The charged molecules migrate through the gel toward one of the electrophoresis electrodes until protonation or deprotonation within the pH gradient results in a net neutral charge for the molecule. A Multiphor II system, purchased from Amersham Pharmacia Biotech, was used. Typically, sample detection within the gel was made using liquid scintillation counting. The gel was sectioned into 1cm sections and each section was put in a glass liquid scintillation vial with 3 ml 0.1% sodium dodecylsulfate (SDS). The SDS solution worked as a detergent to wash the molecules out of the gel matrix which greatly increased counting recovery of the radiolabels. The gel sections were allowed to soak in the SDS solution for 24 hrs. before liquid scintillation fluid was added and the vials counted.

Isoelectric focusing results are given in Table 14, and Figure 7. These results reveal that ^{14}C -labeled colloidal organic matter rich in carbohydrate moieties exhibits strong functional groups with pK_a of 3.5 or less, imparting these colloids a negative charge, and therefore, allowing the majority of organic matter to migrate to the anode ($\text{pH} \leq 3.5$). Furthermore, ^{59}Fe -labeled iron hydroxides and clay minerals were apparently still positively charged, and thus, were able to migrate to the cathode at $\text{pH} \geq 9.5$. In summary, the gel electrophoresis results support our contention that the majority of the colloids is composed of organic matter (^{14}C -labelled) with strong acid, and inorganic clay and iron oxide minerals (^{59}Fe -labelled) with basic functional

groups. Results from 2000 are in agreement with those from 1999, and any differences between the two sets of measurements are small.

Transmission Electron Microscopy (TEM) combined with Energy Dispersive X-Ray Microprobe Analysis (EDAX) were applied to obtain information on composition and forms of colloid samples. Aliquots of freeze-dried colloids (RF137 and RF157) were analyzed by Marcia West and Gary Leppard at McMaster University. Major findings: The main colloids in both samples were clays (some of which contained Fe), microbes (mainly bacteria), microbe parts, debris, biogenic silicates, membranous structures (probably biological), titanium microcrystals and extremely small colloids aggregated into complex structures. These latter aggregates of extremely small colloids could not be properly analyzed morphologically because the samples had been processed as dehydrated powders. Thus the fractal arrangements and long range associations would almost certainly have been artifactually altered (see earlier work of Buffle and Leppard).

The freeze-drying method that was employed can clump the colloids severely, making fine distinctions between the two samples more difficult to ascertain. Likely, sample RF157 was more mineralized than sample RF137, which is corroborated by the metal analysis of the colloid species (Table 9). Sample RF157 was richer in Fe-containing clays than was RF137 (Appendix 4), in agreement with the analytical data (Table 9).

4.3. $^{238}\text{U}/^{234}\text{Th}$ disequilibrium to derive thorium scavenging and particle residence times in Pond B-5:

Measurements of Th(IV), as an analogue of Pu(IV), in total, dissolved and particulate fractions of Pond B-5 water resulted in estimates of how long, on the average, it would take for a four-valent ion to be scavenged and removed from the water. Results of these measurements indicate that the ^{238}U concentrations in Pond B-5 were $2.28 \pm 0.04 \mu\text{g/L}$ ($0.76 \pm 0.01 \text{ pCi/L}$) in unfiltered water, $2.11 \pm 0.11 \mu\text{g/L}$ ($0.71 \pm 0.04 \text{ pCi/L}$) in $0.5 \mu\text{m}$ filtered water; the ^{234}Th concentration in the $0.5 \mu\text{m}$ filter-passing fraction was equal to or less than 0.005 pCi/L , three times our detection limit, while the particulate ($\geq 0.5 \mu\text{m}$) $^{234}\text{Th}_p$ was about 0.04 pCi/L or less (Table 15).

From these activity determinations, the scavenging and particle residence times (τ_i) can be determined, as follows:

$$\tau_i = \tau_{234} \times ([^{234}\text{Th}_i] / \{ [^{238}\text{U}] - [^{234}\text{Th}_i] \}), \quad (1)$$

where i = total, dissolved, or particulate (Baskaran et al., 1996; Santschi et al., 1999).

With $\tau_{234} = \lambda_{234}^{-1}$, λ_{234} = decay constant of $^{234}\text{Th} = 0.03 \text{ d}^{-1}$, $[^{234}\text{Th}_i]/[^{238}\text{U}]$ = activity ratio.

Removal residence times of total, dissolved and particulate ^{234}Th from the water and of ≤ 1 days, ≤ 6 hours and 12 hours, respectively (Table 16), were calculated from our measured ^{238}U and ^{234}Th activities in the water given in Table 15. These short residence times confirm the high efficiency of the holding ponds for particles, and particle-reactive elements such as Pu.

From these results, we would predict that at water residence times in excess of one to a few days, most of the Pu and particle load entering a pond would be removed to the sediments. Water residence times are currently more than a month. If holding ponds were to remain, they should be designed with water residence times of more than a few days to maximize their effectiveness in reducing particle and actinide loads to down stream sites.

4.4. Colloidal Pu release potential from soil resuspension experiments:

Soil resuspension experiments were done with 0.5g of the fine fraction (<1mm) of RFETS soil (726 ± 68 pCi/g $^{239,240}\text{Pu}$, 4.9% OC) in 190 ml of filtered tap water. These experiments demonstrate that Pu that is released during these experiments is mostly of colloidal nature (Table 17). Colloidal Pu is occurring as a pseudo-colloid, i.e., Pu associated with a different carrier phase. As shown in Figures 8 and 9, colloidal Pu concentrations increase over a resuspension time of 1-7 days, in the presence and absence of additional humic acid (at 59.2 mg DOM/L = 24.3 mg-C/L of DOC). Thus, there is a significant kinetic effect during the release of colloidal Pu. When the results from the control experiment are compared with those with increasing Aldrich humic acid (41% OC) concentrations, it becomes clear that colloidal Pu concentrations significantly increase with increasing humic acid concentrations. Soil humic acids extracted from uncontaminated Rocky Flats soils (using the procedure given in appendix 3) contained 16% OC. The soil extracted humic acids turned out to be considerably more effective than the commercial Aldrich humic acids in remobilizing Pu from contaminated soils into the water, given that concentrations are expressed in dissolved organic carbon, DOC, rather than dissolved organic matter (Figures 10 and 11). DOC concentrations in soil solutions (but not in streams), and organic carbon of suspended matter can be of similar magnitude as the concentrations that were used in these lab experiments. Also, pH values during soil resuspension experiments did not change by more than a few tenths of a pH unit, i.e., pH increased from 8.2 to 8.6 in the Controls and 8.5 to 8.6 in the presence of commercial and extracted humic acids (120ppm), after three days of resuspension.

There was only a small difference between the control and alginic acid (Figure 12), regardless of the concentration range, when similar resuspension times were compared. Soil resuspension experiments with the bacteria-derived acid polysaccharide Xanthan, revealed that it acts as a particle-glue, i.e., it exhibited strong particle aggregation effects (e.g., strong filter clogging), but showed insignificant effects on the colloid production potential of resuspended soils, which is consistent with its particle aggregating effects. Its strongest effects is thus on increasing the cohesiveness of particles.

When results at different suspended particulate matter concentrations, after 4-5 days of resuspension, are compared, it is apparent that Pu remobilization is inversely proportional to the soil particle-water ratio (Figure 13). The ratio of resuspended soil to water is thus an important parameter in predicting Pu colloid formation. The phase partitioning coefficient (R_p {in L/kg} = ratio of particulate concentration {in pCi/kg} to the filter-passing concentration {in pCi/L}) for Pu was inversely proportional to suspended particulate matter concentration (C_p , in kg/L), with $R_p = 10^{3.2} C_p^{-0.74}$, or $\log(R_p) = 3.2 - 0.74 \log(C_p)$ (Figure 13). The observation of R_p being a function of particle concentration is consistent with the presence of colloidal Pu in the filter-passing fraction, and is called "particle concentration effect". This phenomenon was previously ascribed to the presence of colloidal species of the analyte, e.g., for Th(IV) and other particle-reactive metals (e.g., Honeyman and Santschi, 1988, 1989). It suggests that higher colloidal Pu concentrations are also found at times of greater amounts of resuspended soils in the water. Even though such an effect might be caused by an organic matter sub-fraction, this particle-concentration effect is much smaller for organic matter itself (Figure 14).

The particle-concentration-effect is, however, also evident from the field samples we collected in 1998 to 2000 (including data from Santschi et al., 1998, 1999b, see Figure 13). Field-derived R_p values for Pu in GS10 and GS03 waters are, however, lower at equivalent suspended matter concentrations (C_p), possibly due to differences in organic matter content and/or physical forms of Pu (particle size distribution). It suggests that Pu in soils further away from source areas

might be in a more "weathered form", i.e., they are associated with finer particles and colloids. As a consequence, colloidal fractions of Pu in field samples amount to 30-70 % of the total Pu in the field samples, at suspended matter concentrations of 30 - 120 mg/L, with the remainder in the particulate fraction. Despite the lowering of the R_p value with increasing C_p concentration, only 0.1 - 1 % of the Pu was remobilized from the soil collected near the 903 Pad (Figure 15). Similar proportions of Pu were remobilized with increased DOC concentrations.

While it is true that most of the relatively high Pu concentrations are coincident with high suspended matter concentrations, which contain 0.1-1 pCi/g of Pu, a much greater proportion of Pu in samples from GS03 and GS10 is in a colloidal rather than particulate form. As mentioned before, this might be due to more weathered Pu further away from sources, and more particulate forms of PuO_2 near the 903 Pad, the site where the soil for the laboratory experiments was taken. It is also likely that in the field, the quality (i.e., composition, e.g., humic acids vs aquagenic organic matter such as acid polysaccharides), in addition to the quantity of DOC, will play an important role in remobilizing Pu from soils.

Regardless, soil resuspension experiments suggest that colloidal Pu release during soil erosion events increases as a function of

- a) suspended particulate matter concentration,
- b) resuspension time, and
- c) humic acid (DOC) concentrations.

Which one of these is the dominant factor in the field will require further analysis of field data.

Pu release from resuspended particles slightly decreases as a function of alginic acid concentrations in the water. Alginic acid, an excretion product by both algae and bacteria in soil and water, has an aggregating effect on particles, while humic acids, the main degradation product of plant matter in soils, generally has a dispersing effect.

These results thus suggest that the addition of colloidal Pu from sediment resuspension and soil erosion to stream water during pond discharge and storm run-off could increase the total Pu concentration, over that of particulate Pu alone, by a factor of 2-4. The increase depends on the amount of eroded soil particles in suspension, the length of time the soil is resuspended, as well as the humic acid concentration of the soil. This conclusion is in agreement with all the field data, which show a good correlation between total Pu concentrations and TSS (total suspended solids, C_p) in the water at most measuring stations. Scatter around the least squares line is approximately around a factor of 2-4, which can be produced by having colloidal Pu, in addition to particulate Pu, in the water rather than only variable Pu concentrations in suspended matter.

4.5. Implications of soil erosion studies: Importance of organic matter for Pu remobilization:

One of the conclusions of the soil resuspension experiments is that DOC concentrations have a major effect in remobilizing colloidal Pu into solution. DOC concentrations measured in 1998, 1999 and 2000 stream samples varied from 4 to 13 mg C/L, with no obvious correlation with Pu concentrations. This could, however, have been due to compositional differences of DOM between spring and summer, aquagenic vs pedogenic organic matter. Furthermore, both quantity as well as the quality of DOC in soil solutions could indirectly affect the extent of soil aggregation/disaggregation, and thus, of Pu remobilization.

5. Conclusions

1. Pond and storm discharge samples collected in spring 2000 showed low Pu concentrations, with a large fraction of the Pu (~90 %) associated with suspended particulate matter, and the 0.5 μm filter-passing fraction of Pu being mostly in colloidal forms. Clay- and organic matter - rich colloids are present in different sizes, as was evident from elemental analyses and TEM and EDAX images.
2. Scavenging and particle residence times in Pond B-5, derived from measurements of $^{238}\text{U}/^{234}\text{Th}$ disequilibria in the water, were of the order of a less than 4 hours to 1 day or less, respectively, supporting the effectiveness of the ponds in reducing particle and Pu loads. From these results, we would predict that at water residence times in excess of one to a few days, most of the Pu and particle load entering a pond would be removed to the sediments. Water residence times are currently more than a month. If holding ponds were to remain, they should be designed with water residence times of more than a few days to maximize their effectiveness in reducing particle and actinide loads to down stream sites. While these short Th(IV)-derived residence times are typical for aquatic systems with suspended particulate matter concentrations of 1-100 mg/L, more measurements are needed to relate Th(IV)-derived residence times to prevailing suspended particulate matter concentrations.
3. Soil resuspension experiments suggest that Pu release during soil erosion events increases as a function of a) suspended particulate matter concentration, b) resuspension time, and c) humic acid (DOC) concentrations. Pu release from resuspended particles slightly decreases as a function of alginic acid (an excretion product of algae and bacteria) concentrations in the water. Soil resuspension experiments were conducted at DOC concentrations typical of soil solutions, but elevated compared to typical stream concentrations. Humic acids extracted from Rocky Flats soils were considerably more effective than commercially available Aldrich Humic Acid in remobilizing colloidal Pu from Rocky Flats soils into the water. These results suggest that higher colloidal Pu found in stream water during pond discharge and storm run-off could be regulated by the length of time the soil is resuspended, as well as the humic acid concentration of the soil. Soil resuspension experiments with the bacteria-derived acid polysaccharide Xanthan may act as a particle-glue, i.e., exhibited strong particle aggregation effects (e.g., strong filter clogging), but showed only insignificant effects on the colloid production potential of resuspended soils, consistent with its more aggregating nature. Its strongest effects is thus in increasing the effective particle size of aggregates, thus reducing soil erosion, rather than in reducing the colloidal Pu production of already resuspended soil.
4. The ratio of resuspended soil to water is also important in regulating Pu colloid formation. The phase partitioning coefficient, R_p (in L/kg), was inversely proportional to suspended particulate matter concentration (C_p , in kg/L), with $R_p = 10^{3.2} C_p^{-0.74}$, or $\log(R_p) = 3.2 - 0.74 \log(C_p)$. A comparison between these soil samples with elevated Pu concentrations and field data from streams at GS3 and GS10 reveals parallel relationships, with lower R_p values in field samples than observed during the soil resuspension experiments. Inverse relationships between R_p and C_p have been described before for Th(IV) (e.g., Honeyman and Santschi, 1988, 1989), and are a consequence of the presence of colloidal forms of Pu in the filter-passing fraction.

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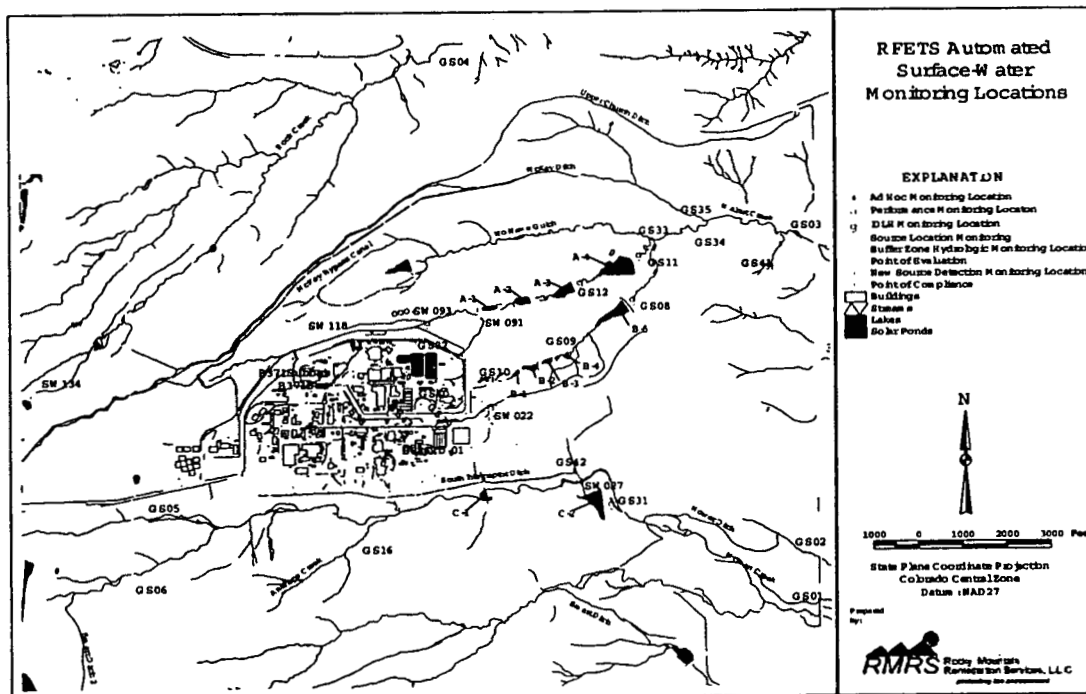


Figure 1. Map of sampling locations, with GS10 at the upstream end of the B Series ponds, and GS03 on Walnut Creek near Indiana Street.

Sampling Setup (all fractions run in duplicate)

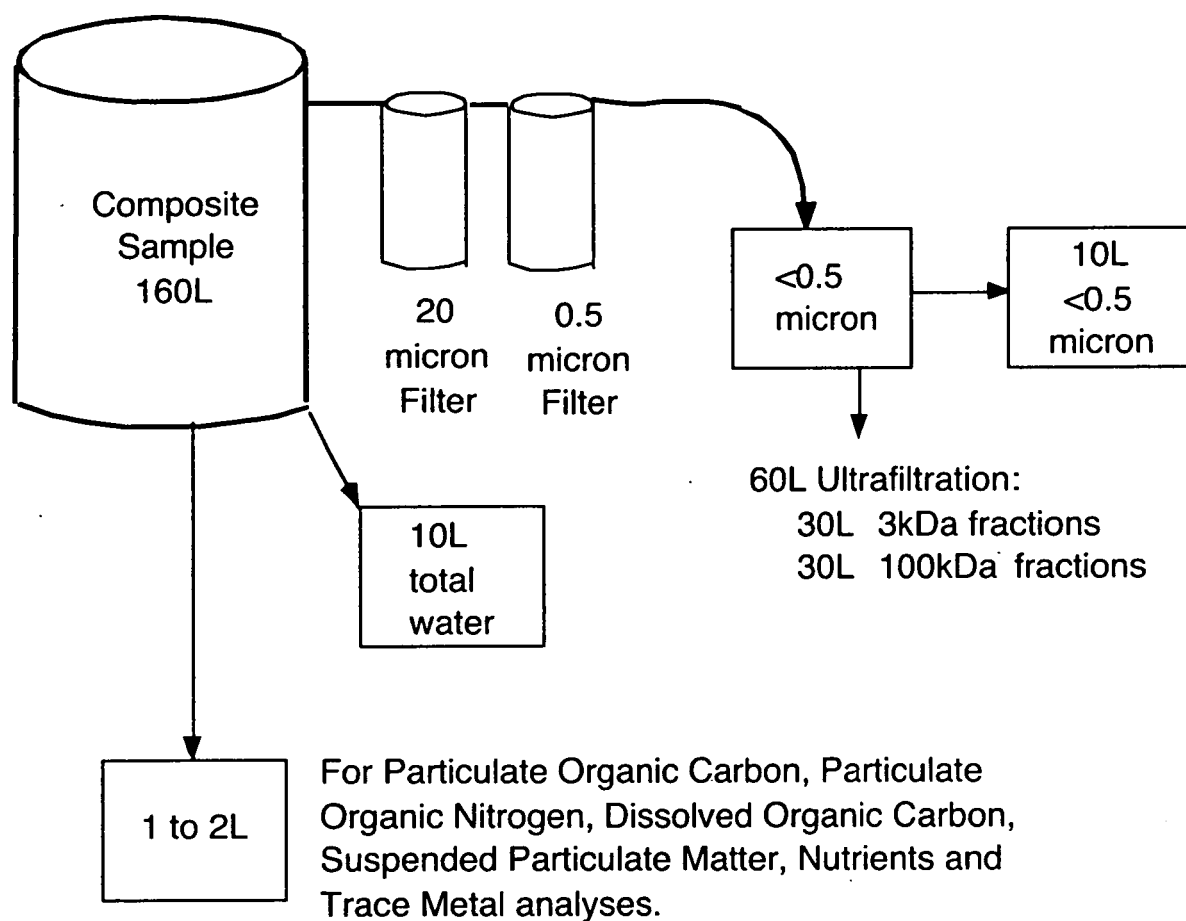


Figure 2. Schematic of field sampling.

Resuspension Experiments

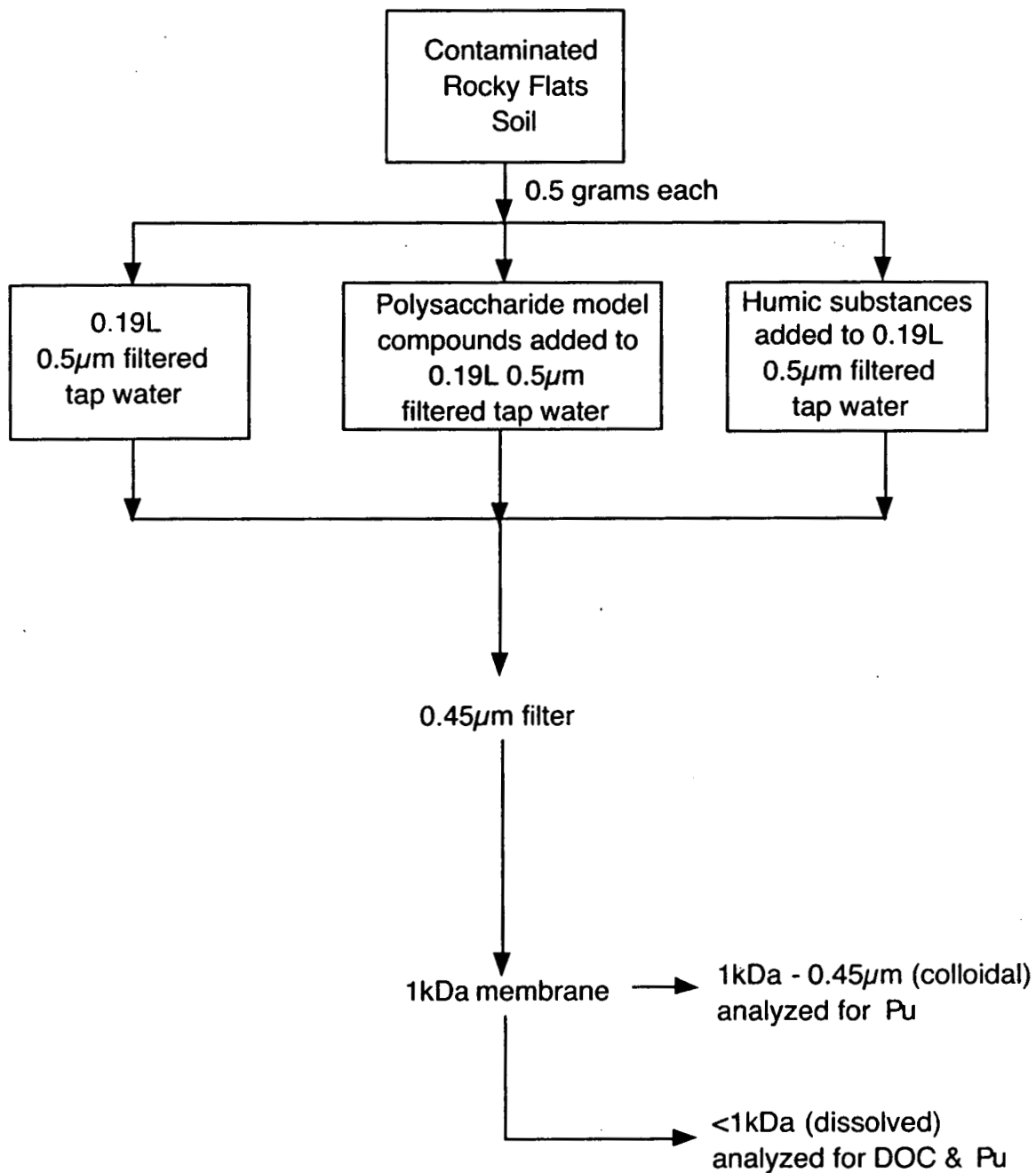
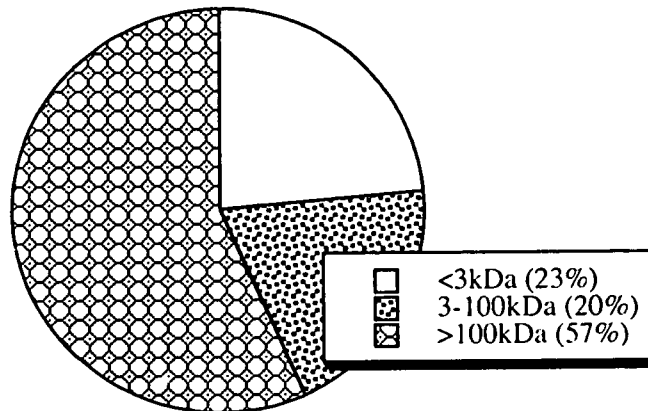


Figure 3. Schematic of soil resuspension experiments. Stirred cell ultrafiltration was only carried out in selected samples.

^{241}Am - Discharge at GS03



^{241}Am - Stormwater at GS10

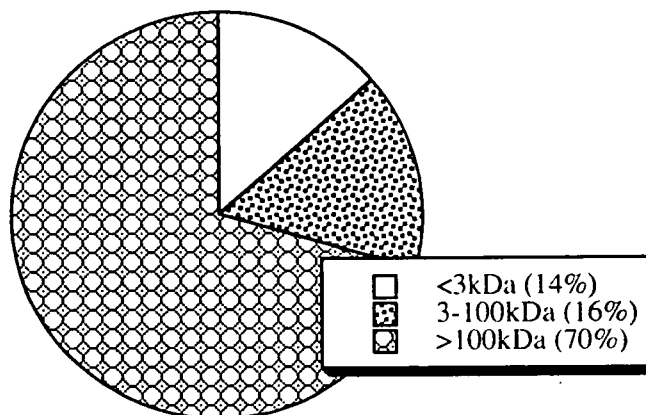


Figure 6. Partitioning of ^{241}Am between ultrafilter-size fractions within the $0.5\mu\text{m}$ filter-passing fraction where <3kDa = measured value, >100kDa = measured 100kDa – $0.5\mu\text{m}$ + 100kDa wash, and 3-100kDa = Total – (<3kDa + >100kDa).

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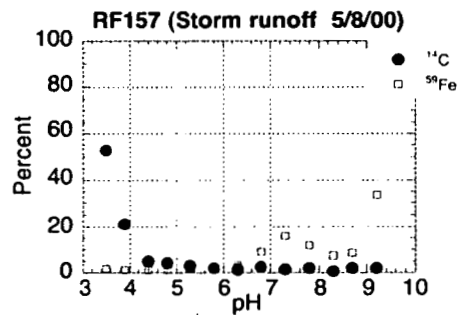
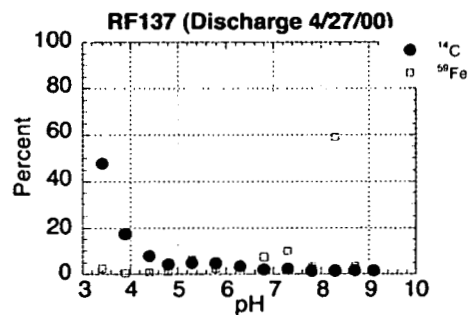
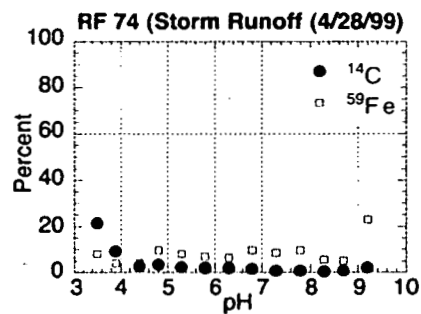
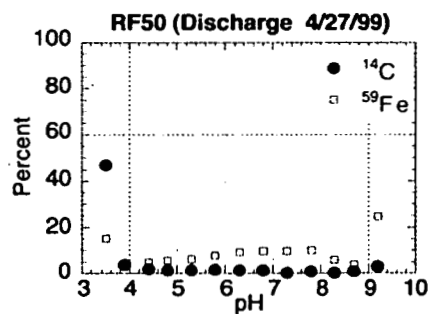


Figure 7. Comparison of gel electrophoresis results for colloids sampled in 1999 and 2000. ^{14}C labels the $-\text{OH}$ sites of sugars which are negatively charged showing strong functional groups with $\text{pK}_a \leq 3.5$. ^{59}Fe labels the $-\text{OH}$ sites of Fe oxyhydroxides and clay minerals which are positively charged with $\text{pK}_a \geq 9.5$.

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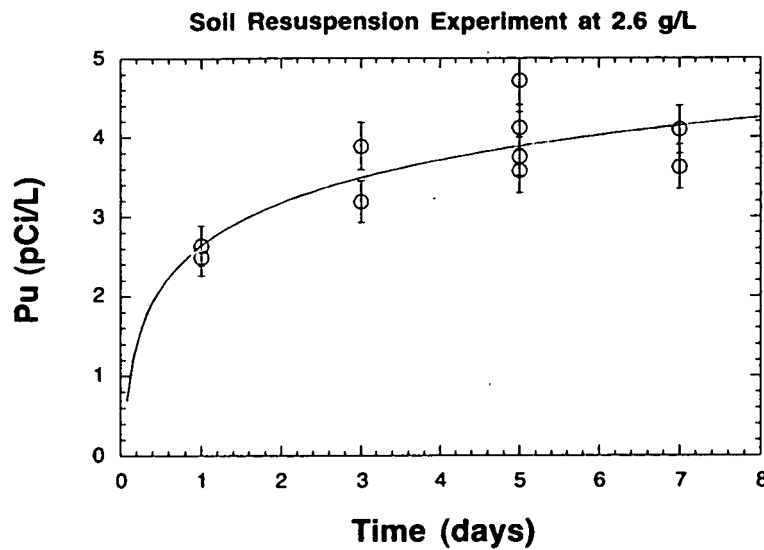


Figure 8. Kinetics of colloidal Pu remobilization during soil resuspension, with no humic acids added. DOC concentrations in solution, resulting from soil resuspension alone, ranged from 2.5 to 2.7 mg/L DOC (0.5 g/190 ml).

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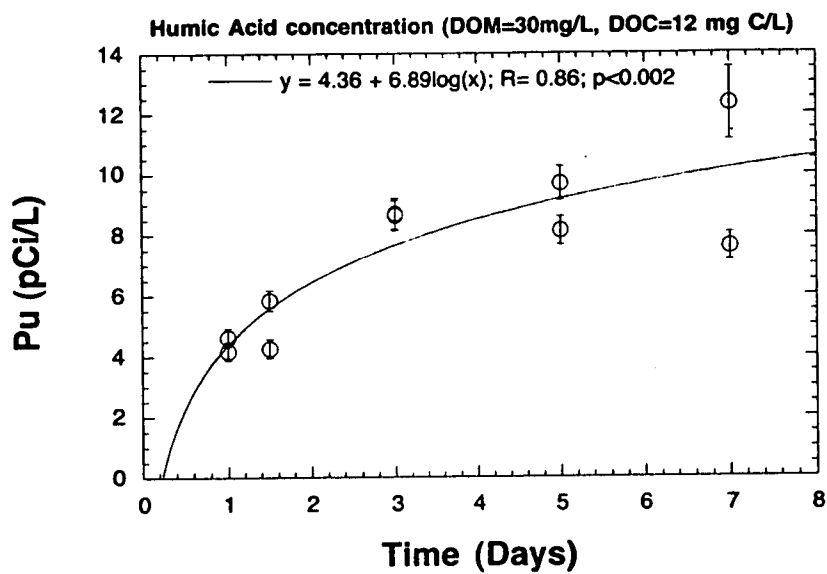


Figure 9. Kinetics of colloidal Pu remobilization during soil resuspension, with a constant amount of Aldrich humic acid added to the experimental solution (0.5 g/190 ml).

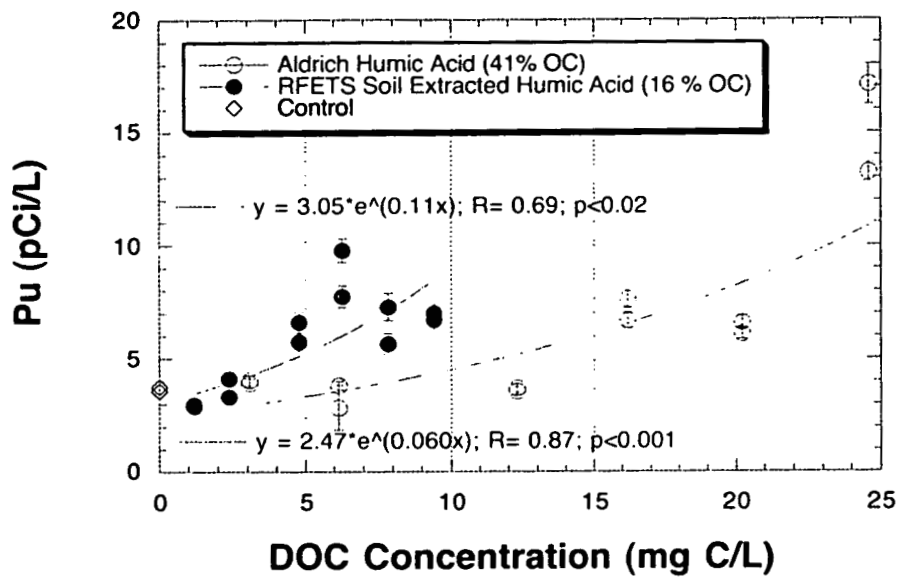


Figure 10. Comparison between Aldrich (41 % OC) and RFETS soil extracted (16 % OC) humic acid additions to the experimental solutions at resuspension times ranging from 3-7 days (0.5 g/190 ml). DOC concentration shown is concentration added to the solution.

22

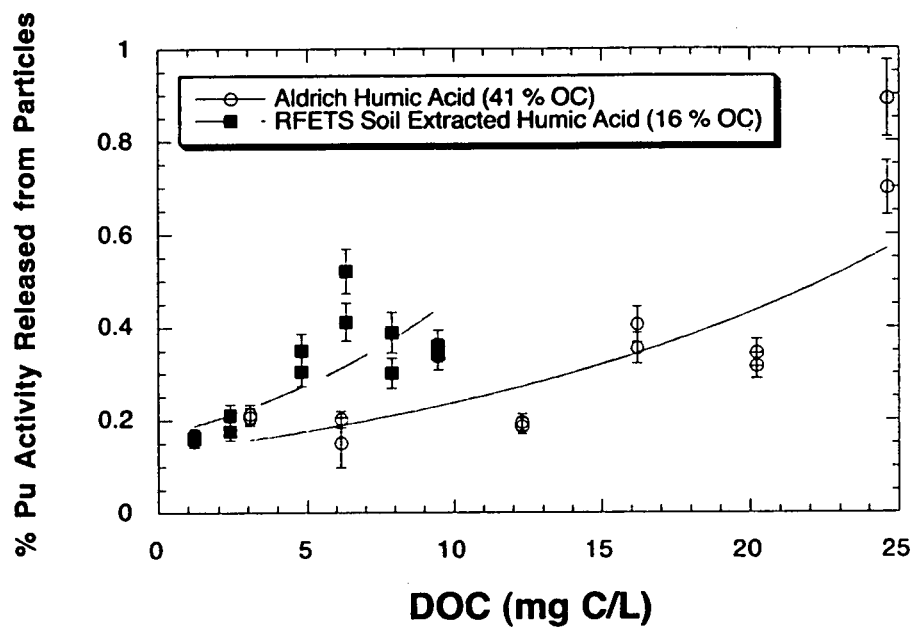


Figure 11. Percent Pu released from the application of different types of humic acids during 3-7 days of soil resuspension (0.5 g/190 ml).

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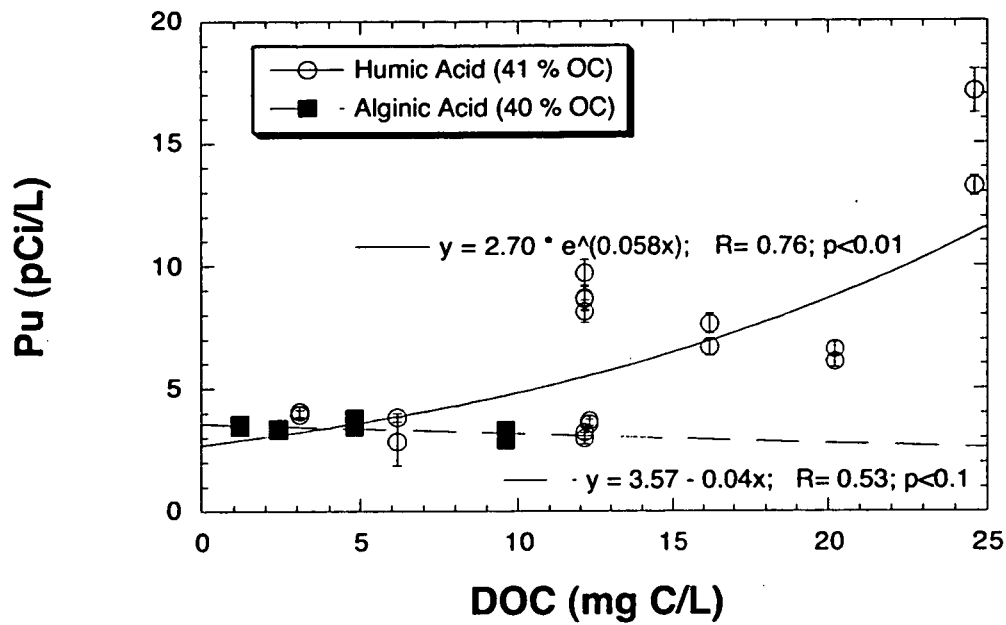


Figure 12. Comparison between Aldrich Humic Acid treated and Alginic Acid treated Pu remobilization experiments by soil resuspension (0.5 g/190 ml).

24

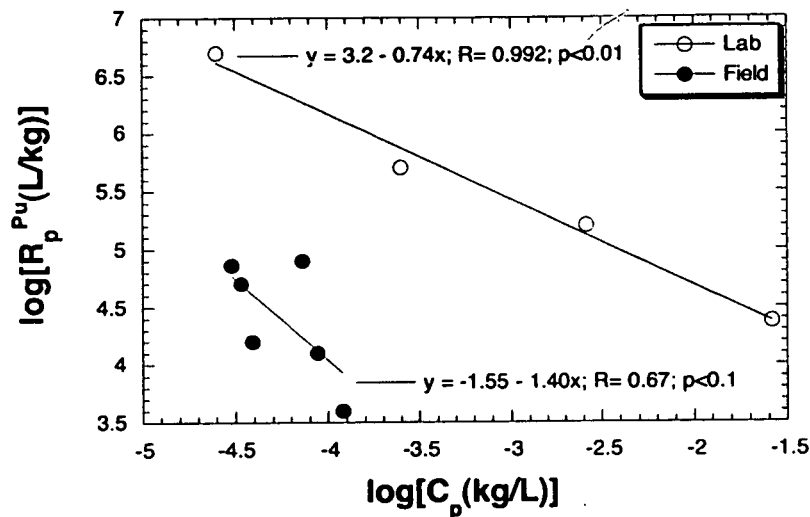


Figure 13. Relationship between total suspended particulate matter (or: solids) concentration (C_p) and phase partition coefficient (R_p) of Pu during soil resuspension experiments, after 4-5 days of particle resuspension, with no additional humic acid added. As Figures 8 and 9 demonstrate, differences between 4-5 days of resuspension are not significant. Laboratory results with RFETS soil taken near 903 Pad are also compared with field results from our water samples taken from GS03 and GS10 during 1998, 1999, and 2000.

25

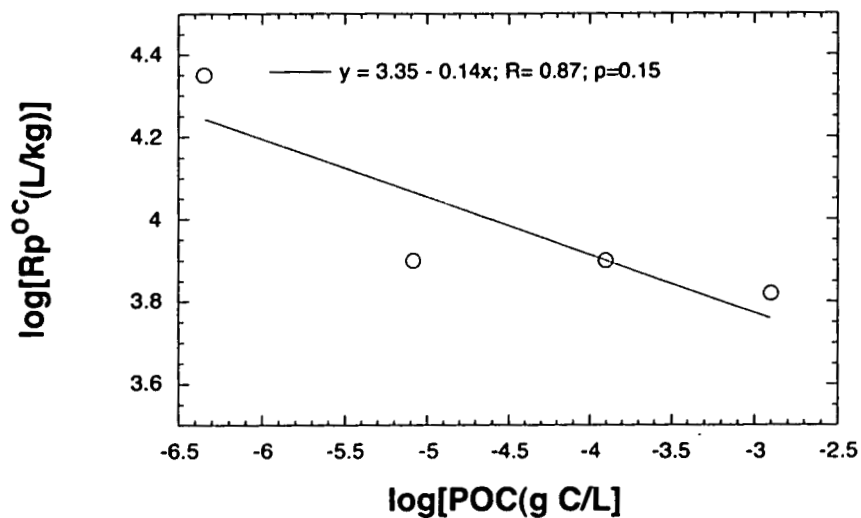


Figure 14. Relationship between total suspended particulate matter (or: solids) concentration (Cp) and phase partition coefficient (Rp) of organic carbon during soil resuspension experiments, after 4-5 days of particle resuspension, with no additional humic acid added.

26

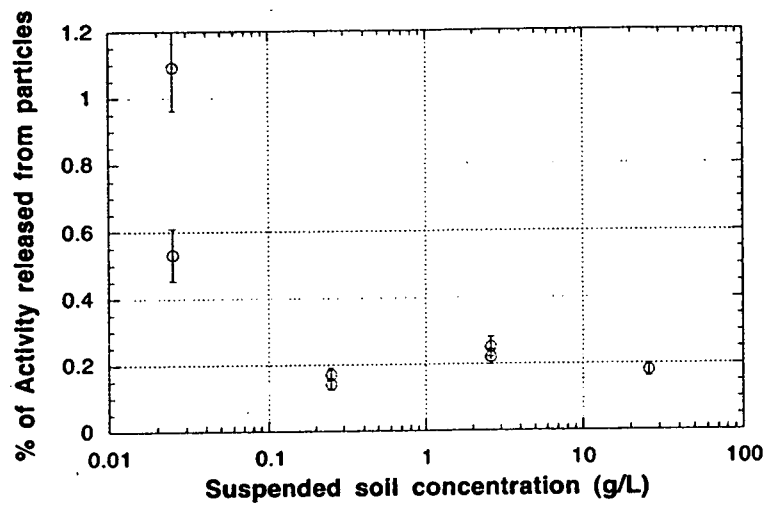


Figure 15. Fraction of soil-bound Pu which is released as a pseudo-colloid during simulated soil resuspension experiments, after 4-5 days of resuspension.

Table 1a. Summary of $^{239,240}\text{Pu}$ in duplicate samples A & B (SD = propagated 1 standard deviation based on α -counting data).

Sample ID	Fraction	A (pCi/l)	SD	B (pCi/l)	SD	Avg	SD
4/27/00 (Discharge)	Total	0.0571	0.0018	-	-	-	-
	<0.5 μm	0.0207	0.0014	-	-	-	-
	>20 μm	-	-	-	-	-	-
	0.5-20 μm	-	-	-	-	-	-
	100kDa-0.5 μm	0.0068	0.0007	0.0006	0.0005	0.0037	0.0009
	<100kDa	0.0038	0.0006	0.0022	0.0008	0.0030	0.0010
	100kDa-Wash	0.0163	0.0006	0.0001	0.0005	0.0082	0.0078
	Sum of Fractions	0.0269	0.0011	0.0029	0.0011	0.0149	0.0016
	3kDa - 0.5 μm	-	-	0.0100	0.0008	-	-
	<3kDa	-	-	0.0131	0.0012	-	-
	3kDa - Wash	-	-	0.0016	0.0006	-	-
	Sum of Fractions	-	-	0.0247	0.0016	-	-

Sample ID	Fraction	A (pCi/l)	SD	B (pCi/l)	SD	Avg	SD
5/8/00 (Storm)	Total	0.0726	0.0043	0.1056	0.0043	0.0891	0.0006
	<0.5 μm	0.0124	0.0013	0.0053	0.0012	0.0885	0.0018
	>20 μm	-	-	0.0773	0.0065	-	-
	0.5-20 μm	0.0828	0.0021	0.0396	0.0016	0.0612	0.0026
	100kDa-0.5 μm	0.0070	0.0006	0.0058	0.0007	0.0064	0.0009
	<100kDa	0.0033	0.0007	0.0041	0.0012	0.0037	0.0014
	100K-Wash	0.0014	0.0005	0.0001	0.0005	0.0008	0.0007
	Sum of Fractions	0.0117	0.0010	0.0100	0.0015	0.0109	0.0018
	3kDa - 0.5 μm	0.0148	0.0012	0.0158	0.0014	0.0153	0.0018
	<3kDa	0.0012	0.0006	0.0007	0.0007	0.0010	0.0009
	3K-Wash	-	-	-	-	-	-
	Sum of Fractions	0.0160	0.0013	0.0165	0.0016	0.0163	0.0021

- = tracer recovery <10%

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Table 1b. Summary of ^{241}Am data in duplicate samples A & B (SD = propagated 1 standard deviation based on α -counting data).

Sample ID	Fraction	A(pCi/l)	SD	B(pCi/l)	SD	Avg	SD
4/27/00 (Discharge)	Total	0.0011	0.0009	0.0026	0.0008	0.0019	0.0012
	<0.5 μm	0.0004	0.0007	0.0003	0.0007	0.0004	0.0010
	>20 μm	-	-	-	-	-	-
	0.5-20 μm	-	-	-	-	-	-
	100kDa-0.5 μm	0.0007	0.0004	-	-	-	-
	<100kDa	0.0022	0.0004	-	-	-	-
	100K-Wash	0.0065	0.0005	-	-	-	-
	Sum of Fractions	0.0094	0.0008	-	-	-	-
	3kDa - 0.5 μm	0.0030	0.0008	-	-	-	-
	<3kDa	0.0030	0.0005	-	-	-	-
	3K-Wash	0.0067	0.0006	0.0029	0.0006	0.0048	0.0008
	Sum of Fractions	0.0127	0.0011	-	-	-	-
Sample ID	Fraction	A(pCi/l)	SD	B(pCi/l)	SD	Avg	SD
5/8/00 (Storm)	Total	0.0602	0.0040	0.0768	0.0033	0.0685	0.0051
	<0.5 μm	0.0017	0.0005	0.0092	0.0009	0.0055	0.0010
	>20 μm	-	-	-	-	-	-
	0.5-20 μm	0.1327	0.0028	0.0406	0.0022	0.0867	0.0036
	100kDa-0.5 μm	0.0030	0.0005	0.0041	0.0004	0.0036	0.0006
	<100kDa	0.0023	0.0005	0.0030	0.0004	0.0027	0.0006
	100K-Wash	0.0031	0.0006	0.0020	0.0004	0.0026	0.0007
	Sum of Fractions	0.0084	0.0009	0.0091	0.0007	0.0089	0.0011
	3kDa - 0.5 μm	0.0106	0.0009	0.0050	0.0004	0.0078	0.0010
	<3kDa	0.0018	0.0006	0.0006	0.0004	0.0012	0.0007
	3K-Wash	0.0009	0.0004	0.0008	0.0004	0.0009	0.0006
	Sum of Fractions	0.0133	0.0012	0.0064	0.0007	0.0099	0.0014

- = tracer recovery <10%

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Table 2. Summary of Pu and Am data used in Figures 4-6.

Sample ID	Size Fraction	^{239,240} Pu	Note	%	²⁴¹ Am	Note	%
		Activity (pCi/L)			Activity (pCi/L)		
4/27/00 Discharge	<3kDa	0.0131	B	49	0.0030	A	23
	3-100kDa	0.0020	#	7	0.0025	#	20
	>100kDa	0.0119	Avg	44	0.0072	A	57
	Total	0.0269	A	100	0.0127	A	100
5/8/00 Stormwater	<0.5μm	0.0053	B	4	0.0092	B	12
	0.5-20μm	0.0396	B	33	0.0406	B	53
	>20μm	0.0773	B	63	0.0270#	#	35
	Total	0.1222	*	100	0.0768	B	100
	<3kDa	0.0010	Avg	6	0.0012	Avg	14
	3-100kDa	0.0081	#	50	0.0014	#	16
	>100kDa	0.0072	Avg	44	0.0062	Avg	70
	Total	0.0163	Avg	100	0.0088	Avg	100

Note: A = from sample 'A', B= from sample 'B', Avg = average of samples 'A' & 'B', # = calculated by difference (total - other fractions), * = sum of fractions. The size fractions are defined as follows: <3kDa = measured, 3-100kDa = Total - (<3kDa + >100kDa), > 100kDa = measured 100kDa - 0.5μm + 100kDa wash.

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Table 3 . Suspended Particulate Matter (SPM, $\geq 0.45\mu\text{m}$) Concentration.

Sample ID	Filter #	SPM (mg/l)	Average (mg/l)	SD	SD (%)
4/27/00-A	8	36.4	34.4	2.8	8.2
"	10	32.4			
4/27/00-B	5	28.8	27.5	1.9	7.2
"	6	25.2			
"	7	28.4			
5/8/00	1	53.6	72.4	16.5	22.8
"	2	84.4			
"	4	79.2			

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Table 4. Particulate Organic Carbon (POC, $\geq 0.7\mu\text{m}$) Concentration.

Sample ID	Filter #	POC (mg-C/l)	Avg(mg/l)	SD	SD(%)
4/27/00	RF021	2.93			
"	RF022	3.29			
"	RF023	3.29	3.17	0.21	6.65
5/8/00	RF015	4.07			
"	RF016	3.96			
"	RF018	4.25	4.09	0.15	3.61

Detection limit = 0.003mg based on three times the SD of the blank values

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Table 5. Particulate Organic Nitrogen (PON, $\geq 0.7\mu m$) Concentration.

Sample ID	Filter #	PON (mg-N/l)	Avg(mg/l)	SD	SD(%)
4/27/00	RF021	0.52			
"	RF022	0.57			
"	RF023	0.63	0.57	0.05	8.98
5/8/00	RF015	0.43			
"	RF016	0.43			
"	RF018	0.43	0.43	0.00	0.00

Detection limit = 0.007mg based on three times the SD of the blank values

Table 6. C/N atomic Ratio of suspended particulate matter ($\geq 0.7\mu\text{m}$).

Sample ID	Filter #	POC(mg/l)	PON(mg/l)	C/N Ratio	Avg	SD	%OC	SD
4/27/00	RF021	2.93	0.52	6.54				
"	RF022	3.29	0.57	6.69				
"	RF023	3.29	0.63	6.14	6.46	0.29	10	1.1
5/8/00	RF015	4.07	0.43	11.13				
"	RF016	3.96	0.43	10.83				
"	RF018	4.25	0.43	11.63	11.19	0.40	5.7	1.3

Table 7. Dissolved organic carbon (DOC, <0.5µm) concentration.

Sample ID	Container #	DOC (ppm)	Avg (ppm)	SD (ppm)
4/27/00	A-1	4.232		
"	A-2	3.648	3.94	0.41
"	B-1	3.733		
"	B-2	3.453	3.59	0.20
5/8/00	A-1	5.094		
"	A-2	5.492		
"	A-3	11.92		
"	A-4	5.384		
"	A-5	5.413	6.66	2.94
"	B-1	5.431		
"	B-2	5.341		
"	B-3	5.082		
"	B-4	5.325		
"	B-5	5.237	5.28	0.13

Detection limit = 0.04ppm based on three times the SD of the blank values

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Table 8. Carbon and Nitrogen (%) in colloids, as average of duplicate measurements.

Sample ID	Description	Size	%C	%N	C/N
RF137	Discharge	3kDa-0.5 μ m	3.10	0.21	14.81
RF147	Discharge	3kDa-0.5 μ m	3.87	0.24	16.52
RF157	Storm	3kDa-0.5 μ m	11.94	0.600	19.88
RF167	Storm	3kDa-0.5 μ m	10.68	0.60	19.88

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Table 9. Trace Metal Concentrations in aqueous (4/27/00 and 5/8/00) and colloidal (RF137, RF147, RF157 and RF167) samples.

Sample ID	Subsample	Fe (ppb)	Al (ppb)	Mn (ppb)
Pond B5	total	45.55	35.24	70.72
	<0.5	26.13	23.34	38.50
	<0.5	26.92	24.55	42.37
	<0.5	26.57	25.84	41.21
4/27/00	A	40.31	15.81	35.14
	B	34.94	14.81	32.30
5/8/00	A	281.41	291.67	19.43
	B	279.67	290.43	21.87

Sample ID	Colloid size	Fe (mg/g)	Al (mg/g)	Mn (µg/g)
RF137	3kDa-0.5µm	0.15	0.07	86.05
RF147	3kDa-0.5µm	0.20	0.16	60.52
RF157	3kDa-0.5µm	10.30	13.32	131.41
RF167	3kDa-0.5µm	8.69	11.91	148.54

Detection limit = 0.030ppb (Fe), 0.34ppb (Al) and 0.05ppb (Mn) based on three times the SD of blank values

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Table 10. Inorganic anion (Cl, NO₃, HPO₄, and SO₄) concentrations.

Sample ID	Subsample	Cl (ppm)	NO ₃ (ppm)	HPO ₄ (ppm)	SO ₄ (ppm)
POND B5	4/26-1	319.03	86.08	0.88	46.74
	4/26-2	293.27	85.67	1.75	42.50
	4/26-3	308.55	85.55	1.0	36.06
	4/26-4	322.89	85.45	1.19	43.03
	4/27-5	314.26	83.47	1.06	37.63
	4/27-6	305.50			29.61
4/27/00	1	>250	7.83	-	61.78
	2	>250	7.71	-	
	3	>250	6.80	-	56.63
	4	>250	7.04	-	57.51
5/8/00	1	>250	28.20	-	7.87
	2	>250	28.35	-	7.93
	3	>250	28.25	-	7.77
	4	>250	28.04	-	7.74

Detection limits = 0.60ppm (Cl), 0.41ppm (NO₂), 0.17ppm (HPO₄), and 0.04 (SO₄) based on three times the SD of the 0.5ppm standard and 0.41ppm (NO₂) based on three times the SD of the 1ppm standard Note: NO₂ Concentrations are below detection limit (BD)

Table 11. Ancillary data taken at time of sampling by site personel.

Parameter	B5 4/26/00	B5 4/26/00	B5 4/27/00	GS03
	10:45	15:25	9:10	4/27/00
pH	9.84	9.95	9.76	8.62
Temperature (°C)	15.3	16.5	13.8	17.6
SC (mS/cm)	1.444	1.391	1.264	1.172
DO(mg/L)	14.47	15.98	14.34	7.62
Alkalinity(mg/L Ca)	110	112.5	100	131

Table 12. ^{239,240}Pu/²⁴¹Am ratios in dissolved, colloidal and particulate samples.

Date	Sample Name	Fraction	Pu/Am-1	SD	Pu/Am-2	SD	Pu/Am-Avg
4/27/00	Discharge	Total	51.91	1.34	-	-	-
		<0.5μm	51.75	6.13	-	-	-
		>20μm	-	-	-	-	-
		0.5-20μm	-	-	-	-	-
		100kDa-0.5μm	9.71	0.57	-	-	-
		<100kDa	1.73	0.05	-	-	-
		100K-Wash	2.51	0.01	-	-	-
		3kDa - 0.5μm	-	-	-	-	-
		<3kDa	-	-	-	-	-
		3K-Wash	-	-	0.55	0.24	-
5/8/00	Storm event	Total	1.21	0.00	1.38	0.08	2.58
		<0.5μm	7.29	0.22	0.58	0.14	7.87
		>20μm	-	-	-	-	-
		0.5-20μm	0.62	0.00	0.98	0.07	1.60
		100kDa-0.5μm	2.33	0.03	1.41	0.22	3.75
		<100kDa	1.43	0.07	1.37	0.44	2.80
		100K-Wash	0.45	0.03	0.05	0.25	0.50
		3kDa - 0.5μm	1.40	0.01	3.16	0.38	4.56
		<3kDa	0.67	0.11	1.17	1.40	1.83
		3K-Wash	-	-	-	-	-

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Table 13. Phase distribution coefficients (R_p , l/kg or ml/g) of $^{239,240}\text{Pu}$ and ^{241}Am .

Isotope	Sampling Date	Sample Name	C_p (mg/l)	R_p (ml/g)
$^{239,240}\text{Pu}$	4/27/00	Discharge	34	$4.8 \cdot 10^4$
$^{239,240}\text{Pu}$	5/8/00	Storm event		
^{241}Am	4/27/00	Discharge	72	$8.0 \cdot 10^4$
^{241}Am	5/8/00	Storm event		

C_p (mg/l) is the concentration of suspended particulate matter.

Table 14. Percent of total activity recovered during isoelectric focusing. ^{14}C labels -OH sugars and ^{59}Fe labels -OH sites of Fe oxyhydroxides and clays.

pH	^{14}C	^{14}C	^{59}Fe	^{59}Fe
	RF137	RF 157	RF137	RF 157
<3.9	47.79	52.90	2.50	1.96
3.9	17.15	20.84	0.45	1.26
4.4	7.67	5.08	0.70	1.29
4.8	4.05	4.09	0.86	1.29
5.3	4.79	3.01	6.49	1.90
5.8	4.79	2.19	2.22	1.97
6.3	3.52	1.34	2.95	3.42
6.8	2.04	2.48	7.29	9.29
7.3	2.44	1.55	9.95	15.99
7.8	1.31	2.17	3.40	11.86
8.3	1.31	0.62	59.06	7.35
8.7	1.64	1.88	3.55	8.74
>8.7	1.51	1.88	0.57	33.69

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Table 15. Results of ^{238}U (ICP-MS) and ^{234}Th (Gamma Spectrometry) measurements of pond B5 water.

Day	#	$[^{234}\text{Th}_d]^*$	$[^{234}\text{Th}_p]$	$[^{234}\text{Th}_i]$ (dpm/L)	$[^{238}\text{U}]$	$[^{238}\text{U}_d]$	$[^{238}\text{U}_p]$
4/26	1	≤ 0.01	0.04 ± 0.008	0.05	1.69 ± 0.03	1.56 ± 0.08	0.13 ± 0.09
	2	≤ 0.003	0.01 ± 0.002	0.013	"	"	"
4/27	1	≤ 0.02	0.03 ± 0.004	0.05	"	"	"
	2	≤ 0.01	0.02 ± 0.002	0.03	"	"	"
Average		≤ 0.01	0.025	0.036	1.69 ± 0.03	1.56 ± 0.08	0.13 ± 0.09

*) Calculated from 3 times base line concentration of ^{234}Th gamma region (63 keV). Value also equal to MDA (minimum detectable activity).

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Table 16. Results of total, dissolved and particulate ^{234}Th residence times in pond B5 water, calculated using eq. 1 (see text).

Day	#	τ_t	τ_d (days)	τ_p
4/26	1	≤ 1.1	≤ 0.22	0.84
	2	≤ 0.3	≤ 0.07	0.21
4/27	1	≤ 1.1	≤ 0.45	0.62
	2	≤ 0.6	≤ 0.22	0.42
Average		≤ 0.8	≤ 0.24	0.52

Table 17: Phase speciation results using a 1kDa stirred cell ultrafiltration after resuspending 0.5g RFETS soil in 190ml of filtered tap water.

	Fraction	pCi/L	SD	%	pCi/L	SD	%
Control	<0.45µm	2.812	0.253		5.547	0.409	
	0.45-1kDa	2.649	0.324	94.21	3.572	0.378	64.40
	<1kDa	1.011	0.209	35.97	0.896	0.153	16.15
	Filter leach	0.004	0.003	0.14	0.013	0.006	0.23
	Sum	3.665	0.386	130.33	4.481	0.408	80.77
Aldrich Humic Acid (59 mg/L)	<0.45µm	7.141	0.507		6.428	0.444	
	0.45-1kDa	4.565	0.430	63.94	4.819	0.506	74.98
	<1kDa	0.152	0.071	2.13	0.368	0.110	5.72
	Filter leach	0.043	0.010	0.60	0.074	0.019	1.15
	Sum	4.760	0.436	66.66	5.261	0.518	81.85

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